Karlsruhe Institute of Technology

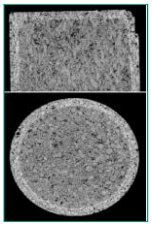
ETH Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich

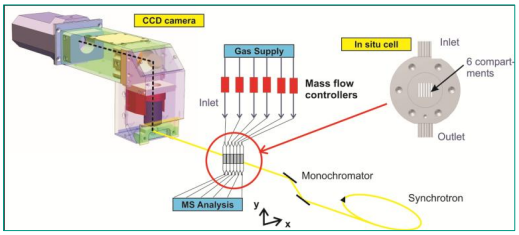
DTU

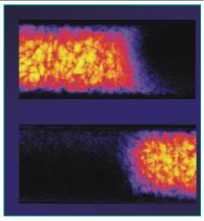
Shining X-rays on Catalytic Reactors: Importance of Time and Spatially Resolved Studies

Jan-Dierk Grunwaldt

Institute for Chemical Technology and Polymer Chemistry, Campus South







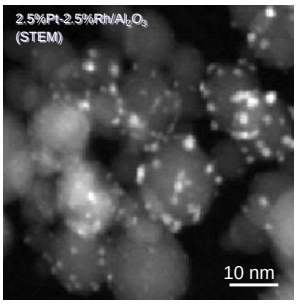
Overview

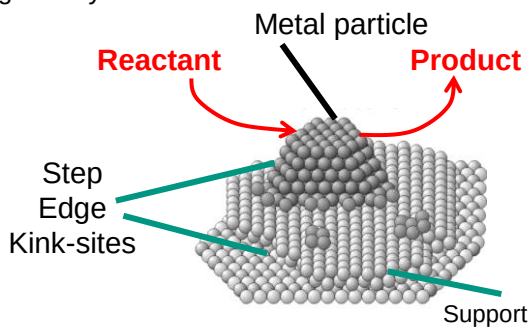
Karlsruhe Institute of Technology

- Introduction: Setting the scene
- Time resolved studies
- Scanning and full-field X-ray microscopy in the µm and mm regime
- Spatiotemporal studies
- Summary and outlook

Imaging a working catalyst – our view

- Improvement of catalysts triggered by the microscale





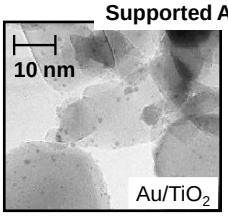
Catalytic Properties ⟷ Physical and electronic properties at an atomic scale

Picture adapted from: J. Libuda, H.-J. Freund

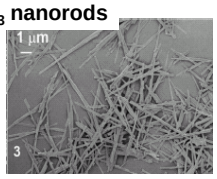
Imaging working catalysts

- Improvement of catalysts triggered by the microscale

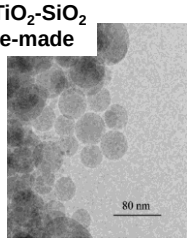
Supported Au-particles



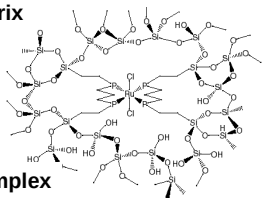
MoO_3 nanorods



1.3%TiO_2-SiO_2 flame-made

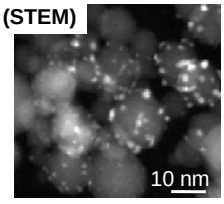


Microcrystalline
Amorphous materials
Molecular species inside a matrix



Ru-complex

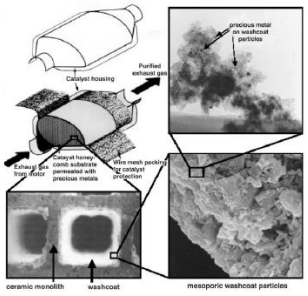
2.5%Pt-2.5%Rh/Al_2O_3 (STEM)



Structure may change under operating conditions

Imaging working catalysts

- Improvement of catalysts triggered by the microscale
- Equally important is the „macroscale“
  - Real catalysts are in large scale fixed bed reactors
    - Pressure drop needs to be minimized
    - Strength of catalyst pellets
    - Optimized diffusion parameters



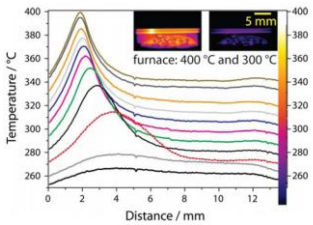
A.T. Bell, Science 299, 1688 (2003)

(Haldor Topsøe)

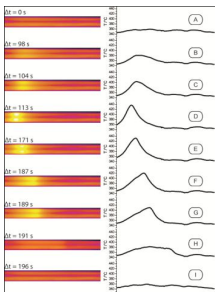
Imaging working catalysts

- Improvement of catalysts triggered by the microscale
- Equally important is the „macroscale“
  - Real catalysts are in large scale fixed bed reactors
    - Pressure drop needs to be minimized
    - Strength of catalyst pellets
    - Optimized diffusion parameters
  - Temperature and concentration gradients in catalytic reactors

Partial oxidation of methane over 2.5%Rh/Al_2O_3



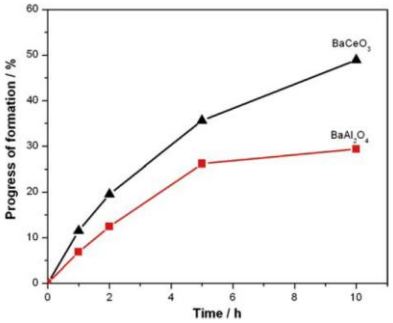
Partial oxidation of methane over Pd

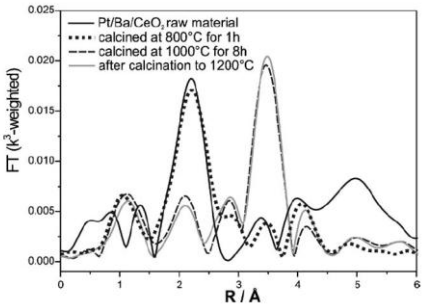


Imaging working catalysts – time resolution

- Long-term dynamic effects
  - Sintering and ageing
  - Restructuring

Formation of $BaCeO_3$, $Pt_xBa_{1-x}CeO_3$ in NSR-catalysts





M. Casapu, J.-D. Grunwaldt, et al., Top. Catal. 42, 3 (2007), J. Catal, 251, 48 (2007)

Imaging working catalysts – time resolution

- Long-term dynamic effects
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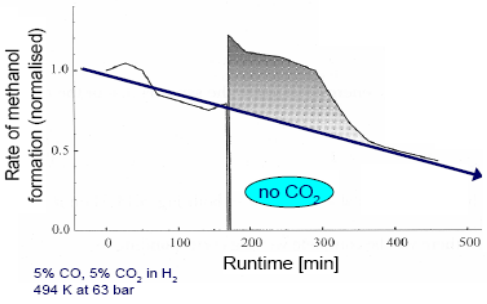
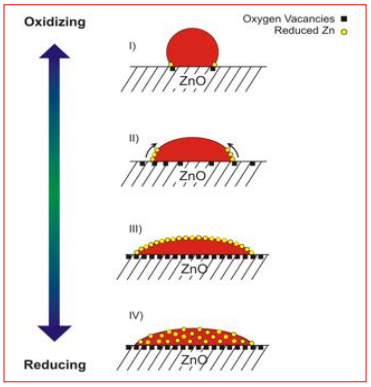


H. Topsoe et al., in Dynamics of Surfaces and Reaction in Heterogeneous Catalysis (1997)

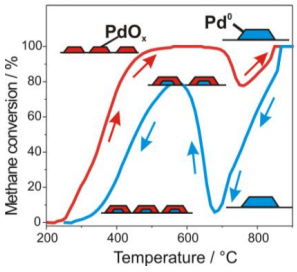


Grunwaldt, Clausen et al., J. Catal. 194, 452 (2000)
Grunwaldt and Clausen, Topics Catal. 18, 37 (2002)
Hansen et al., Science 295, 2053 (2002)

Imaging working catalysts – time resolution

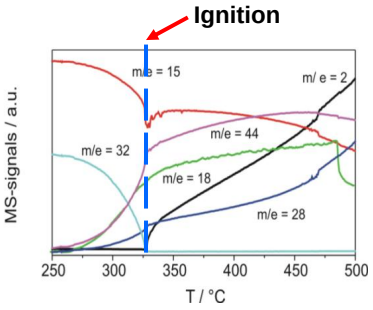
- Long-term dynamic effects
  - Sintering and ageing, restructuring
- Rapid structural changes
  - Temperature programmed reaction
  - Ignition, extinction
  - Oscillating reactions
  - Activation of catalysts (e.g. reduction)

Total oxidation of methane over 10%Pd/ZrO_2



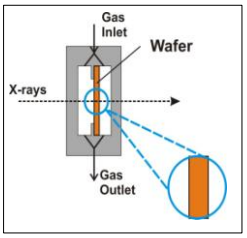
Grunwaldt, et al. Chem. Commun., 4635 (2007).

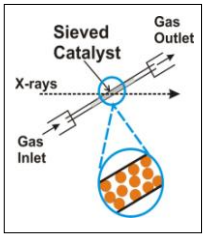
$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$



Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

Shining X-rays on catalysts – best compromise?





$$\tau_{film} \cong \frac{\rho_{CuO} \cdot \frac{d}{2}}{k_m \cdot c_{H2}} \longrightarrow \textbf{6.5 s}$$

$$\tau_{film} \cong \frac{\rho_{CuO} \cdot R_p}{3k_m \cdot c_{H2}} \longrightarrow \textbf{1.7 ms}$$

$D_e=10^{-6}$ to 10^{-8} m²/s

$$\tau_{pore} \cong \frac{\rho_{CuO} \cdot (\frac{d}{2})^2}{2D_e \cdot c_{H2}} \longrightarrow \textbf{0.5 to 60 min}$$

$$\tau_{pore} \cong \frac{\rho_{CuO} \cdot R_p^2}{6D_e \cdot c_{H2}} \longrightarrow \textbf{0.02 to 2 s}$$

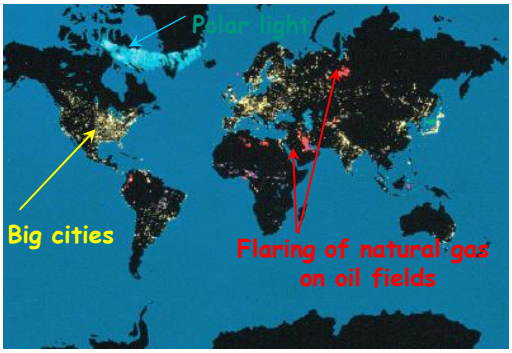
Grunwaldt et al., PCCP **6**, 3037 (2004).

Catalytic partial oxidation of methane

$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$

- **Active Catalysts: Supported noble metals, Ni-catalysts [1]**
- **Alternative route to steam/ autothermal reforming [2]**
- **Synthesis gas for production of liquid fuels**
- **Useful in stationary SOFCs**

Flaring of natural gas

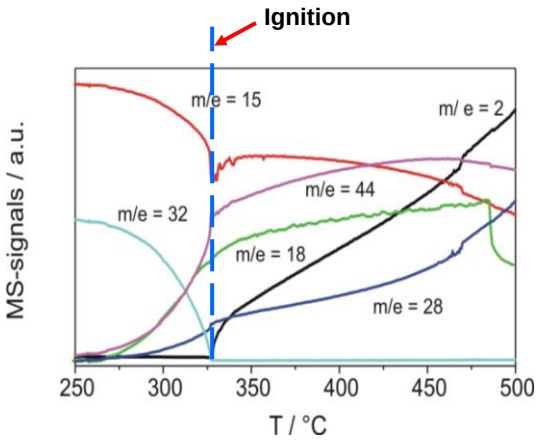


From: L. Plass, S. Reimelt, CIT 79, p. 561 (2007)

[1] A.P.E. York et al., Topics Catal. 22, 345 (2003)
Hickmann and Schmidt, Science 259, 343 (1993)
[2] J.R. Rostrup-Nielsen, J. Sehested, J.K. Norskov, Adv. Catal. 47, 65 (2002)

Catalytic partial oxidation of methane: Ignition of the reaction

$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$

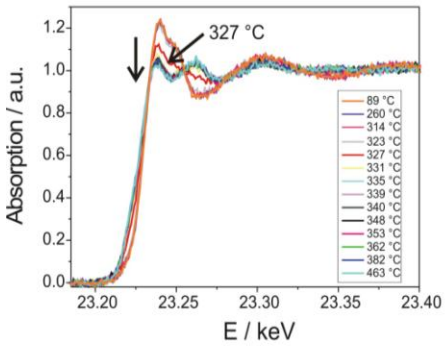


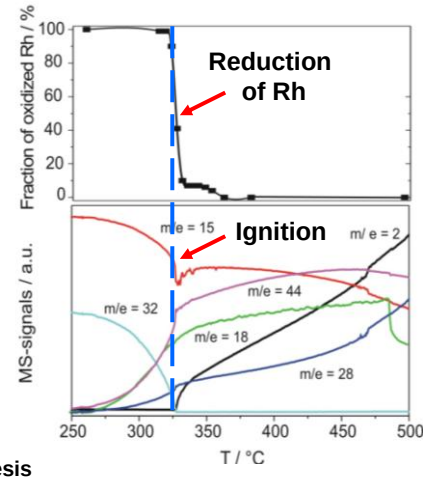
2.5%Rh-2.5%Pt/Al_2O_3, prepared by flame synthesis
6% CH_4, 3% O_2 in He, ramp rate: 5 K/min

Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

Catalytic partial oxidation of methane: Ignition of the reaction

$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$

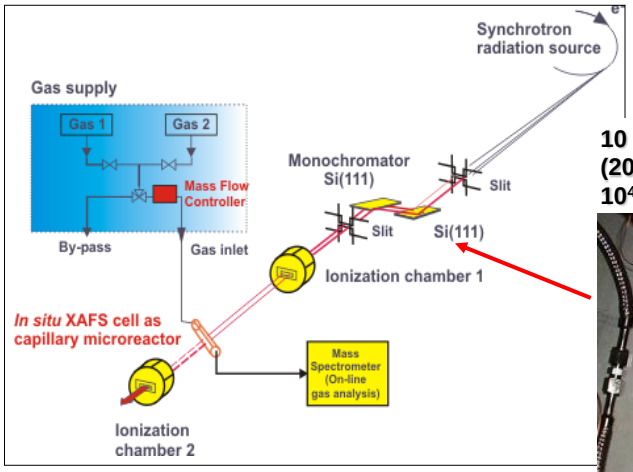




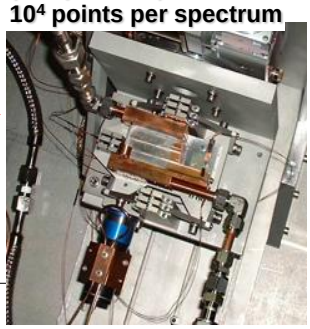
2.5%Rh-2.5%Pt/Al_2O_3, prepared by flame synthesis
6% CH_4, 3% O_2 in He, ramp rate: 5 K/min; linear combination of spectra from starting and end spectrum

Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

Improved time-resolution

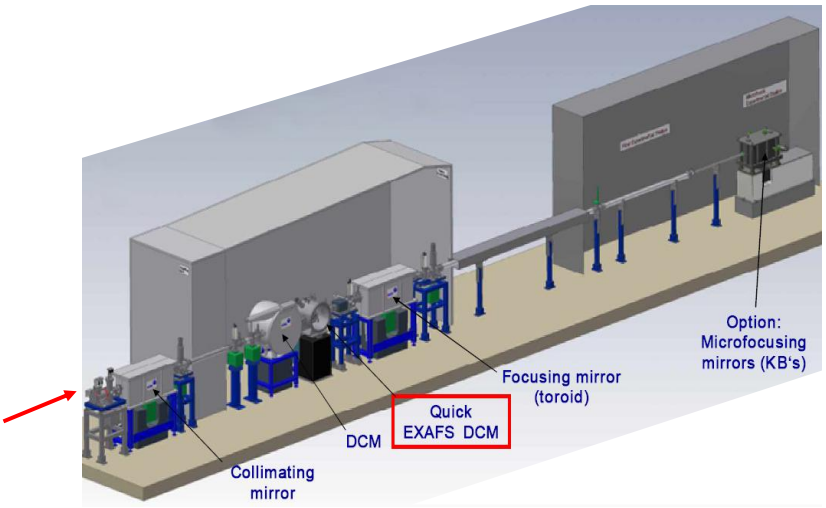


10 full oscillations/s
(20 spectra/s)
10^4 points per spectrum



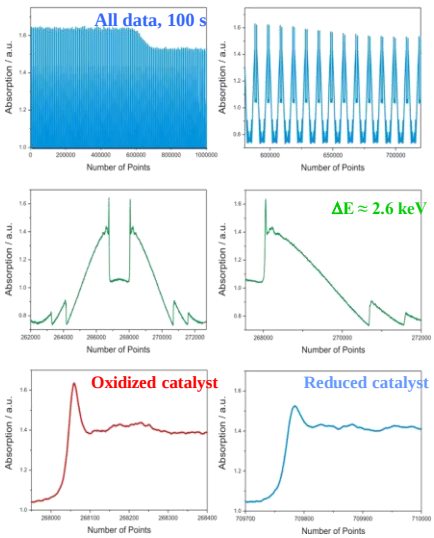
Lützenkirchen-Hecht, Grunwaldt, Frahm et al., Physica Scripta T115, 831 (2005).

Improved time-resolution: Setup at SLS



(Entire beamline delivered and installed by ACCEL)

QEXAFS during the catalytic partial oxidation of methane



Pt L-edges

1 Hz oscillation frequency

⇒ 2 spectra/s

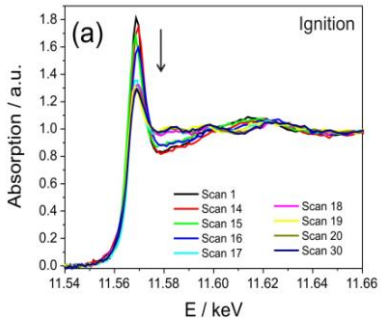
5% Pt -5% Rh / Al_2O_3 catalyst in 6% CH_4 / 3% O_2 / He atmosphere between 321 and 331° C sample temperature.

Data collected at the SLS.

Grunwaldt, Stötzel, Frahm et al., PCCP 11, 8799 (2009).

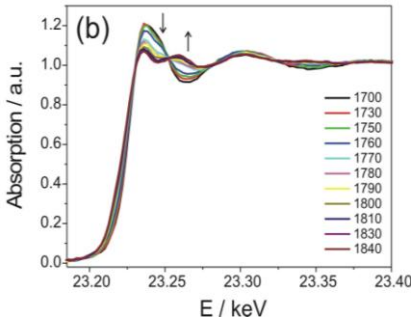
Ignition of the catalytic partial oxidation of methane

Pt L_3-edge



Recorded with Si(111) crystal at SLS with 1 Hz

Rh K-edge

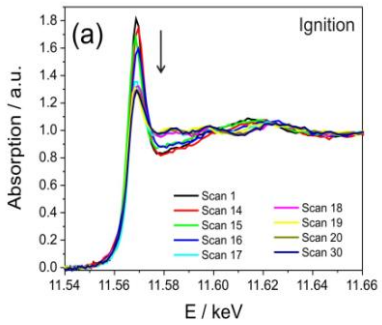


Recorded with Si(311) crystal at APS with 1 Hz

Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He

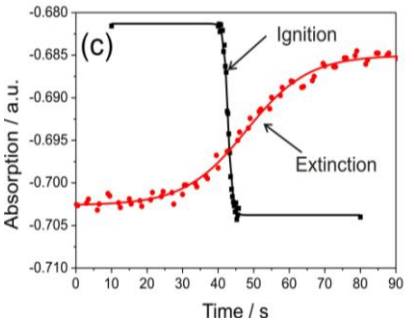
Ignition of the catalytic partial oxidation of methane

Pt L_3-edge



Recorded with Si(111) crystal at SLS with 1 Hz

Results from LCA analysis

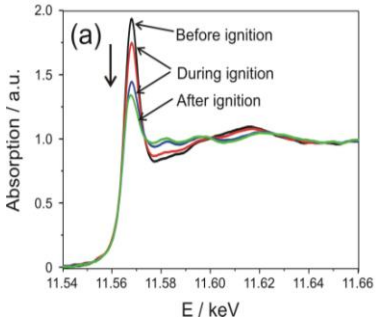


Note: ignition temperature higher than extinction temperature and strongly correlated to hydrogen evolution

Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He

Improved time-resolution by QEXAFS

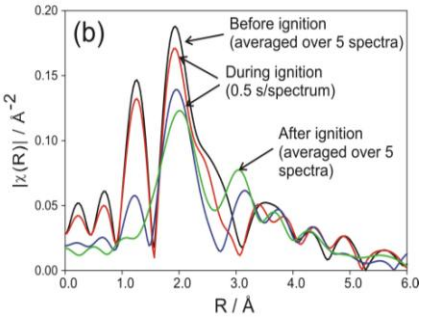
XANES at Pt L_3-edge



Recorded with Si(111) crystal at SLS with 1 Hz

Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He

EXAFS at Pt L_3-edge

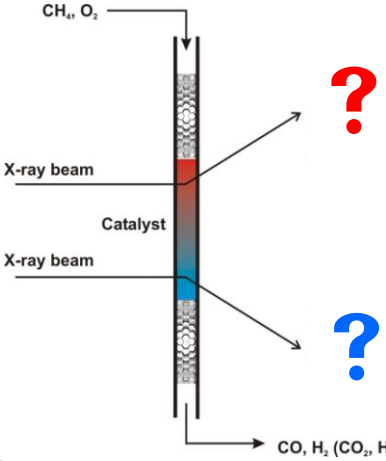


Recently extended to liquid phase (hydrothermal synthesis), improvement of statistics by modulation excitation spectroscopy, etc.

Stötzel, Grunwaldt, Frahm et al., J. Phys. Conf. Ser. 190, 012153 and 012162 (2009)
Zhou, Patzke, Grunwaldt, Frahm, Small, in press.

Monitoring over the catalyst bed during CPO

$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$



Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He, ca. 320 °C

Two mechanisms of partial methane oxidation

Combustion and reforming of methane
$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$ ΔH=-802 kJ/mol
$CH_4 + H_2O \rightarrow CO + 3H_2$ ΔH=+206 kJ/mol
$CH_4 + CO_2 \rightarrow 2 CO + 2H_2$ ΔH=+248 kJ/mol

Direct partial oxidation of methane
$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$ ΔH=-35.5 kJ/mol

Monitoring over the catalyst bed during CPO

$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$

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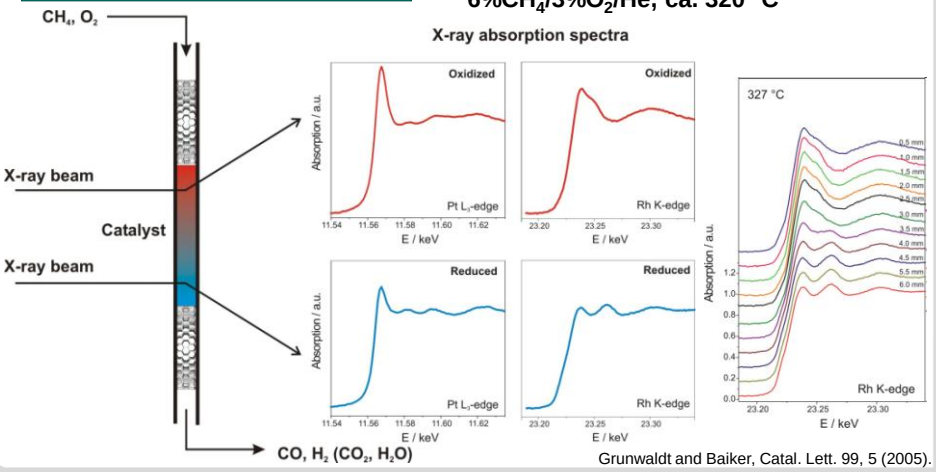

Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

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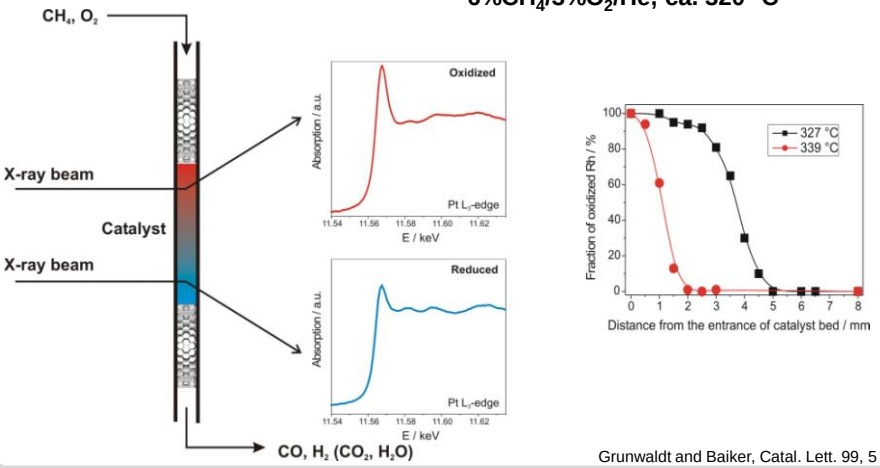

Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

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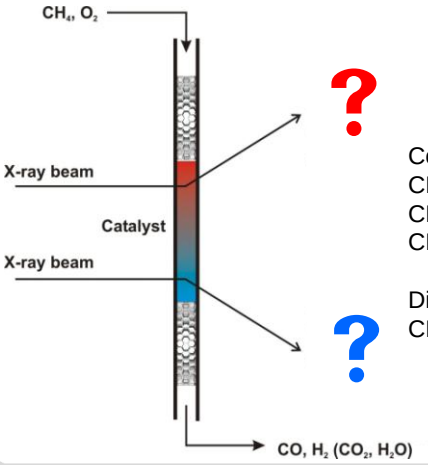

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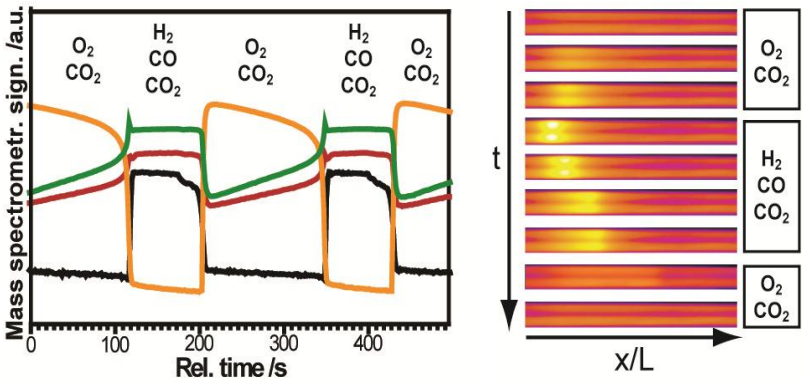
Direct partial oxidation of methane

$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$ ΔH=-35.5 kJ/mol

Partial oxidation of methane over Pd/Al_2O_3

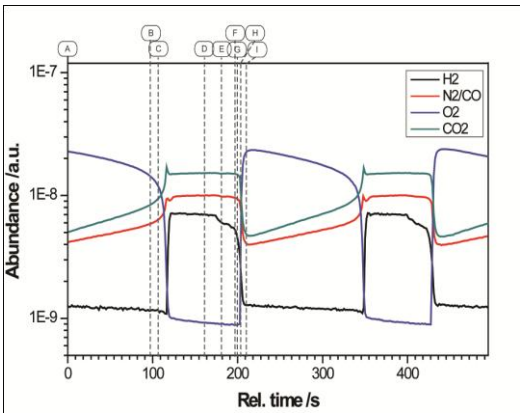
$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$

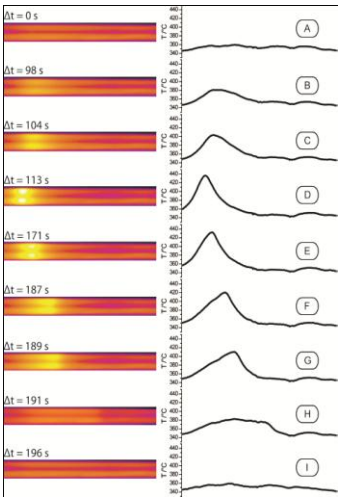
Sample:
5%Pd/Al_2O_3 in
6%CH_4/3%O_2/He, ca. 320 °C



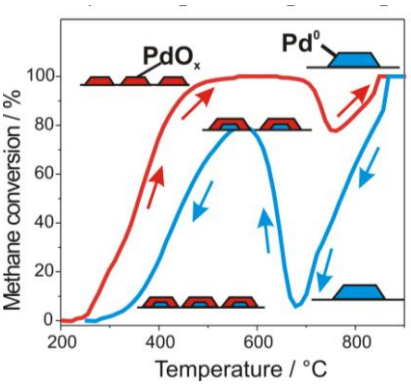
Kimmerle, Baiker, Grunwaldt, PCCP 12, 2288 (2010).

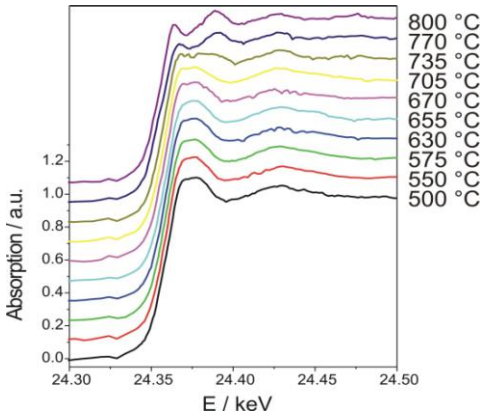
Oscillations during CPO over Pd/Al_2O_3





A look on the total oxidation of methane

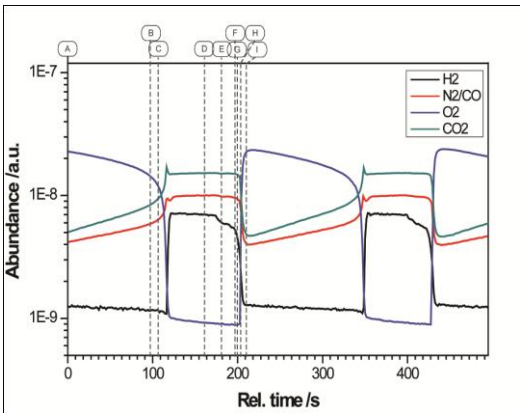


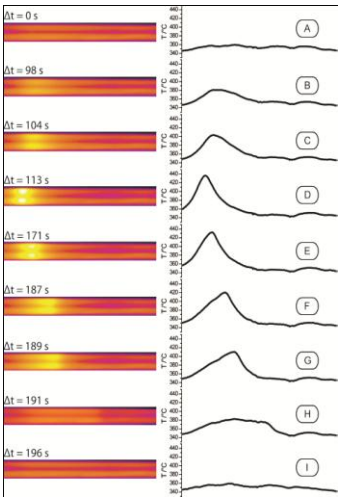


10%Pd/ZrO_2, prepared by flame-synthesis

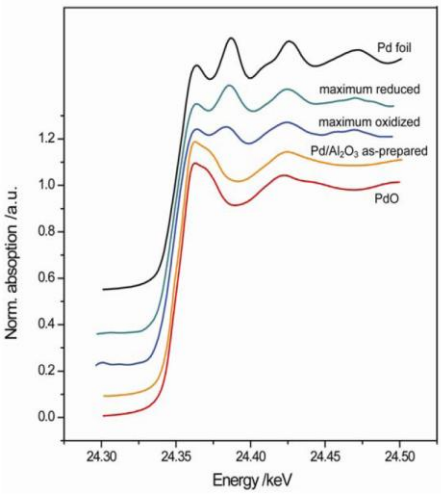
Grunwaldt, et al. Chem. Commun., 4635 (2007).

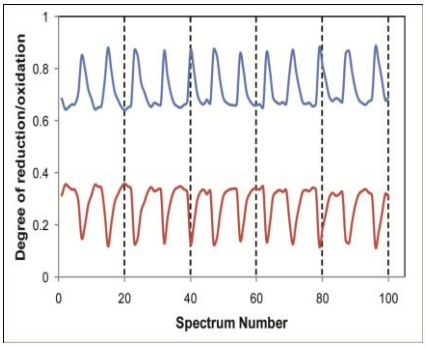
Oscillations during CPO over Pd/Al_2O_3





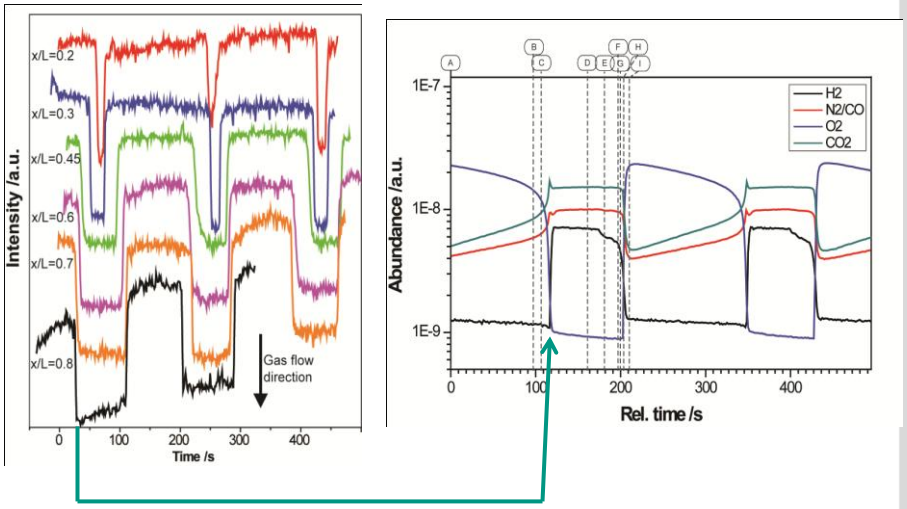
LCA analysis during CPO over Pd/Al_2O_3





Kimmerle, Baiker, Grunwaldt, PCCP 12, 2288 (2010).

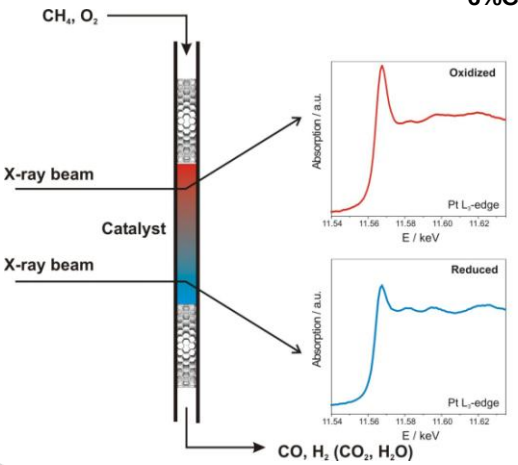
LCA analysis during CPO over Pd/Al_2O_3

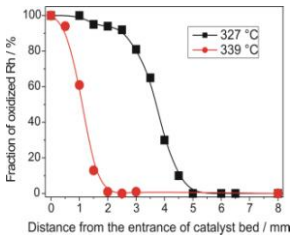


Monitoring over the catalyst bed during CPO

$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$

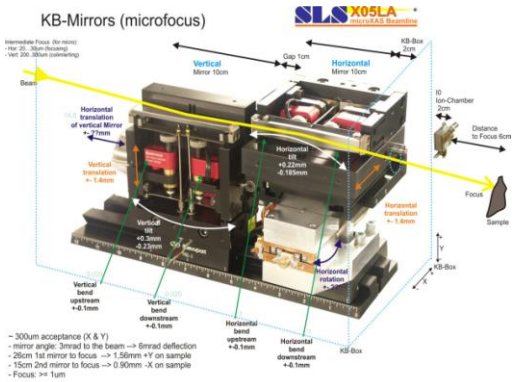
Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He, ca. 320 °C

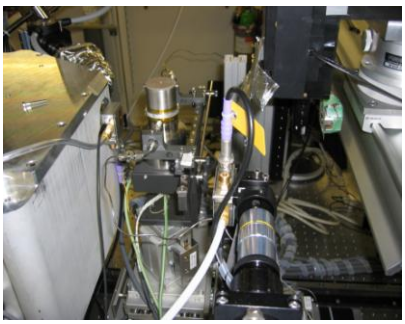




Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

Scanning X-ray microscopy with microfocussed beam

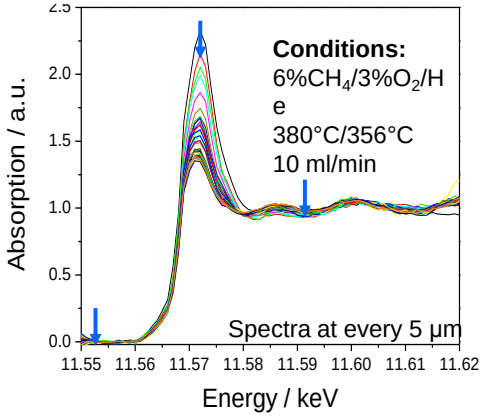




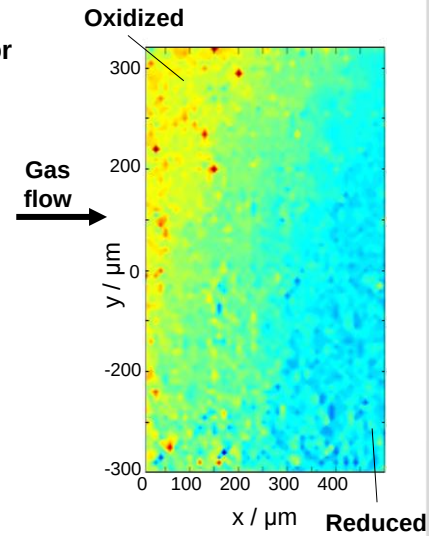
KB-Mirrors at SLS
Focus down to
1 µm x 1 µm

Microfocussed beam: KB-mirrors at SLS

1D-scan in the middle of the microreator

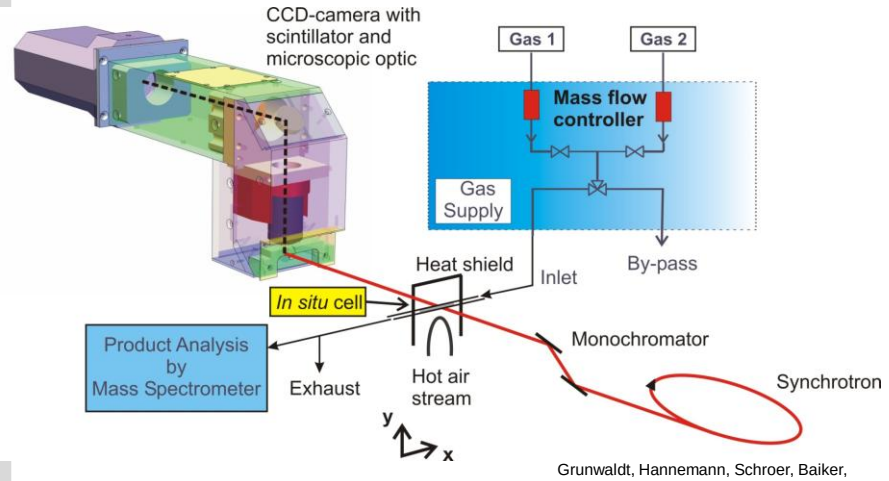


Maps at: 11.555 keV, 11.572 keV, 11.590 keV



J.-D. Grunwaldt, et al., Catal. Today 145, 267 (2009).

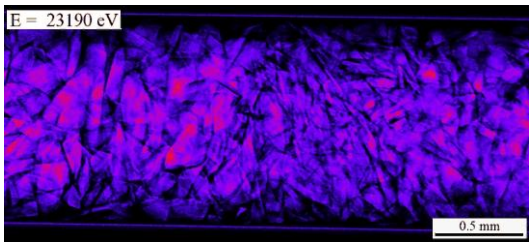
Full field X-ray microscopy: Recording X-ray absorption spectra with an X-ray camera

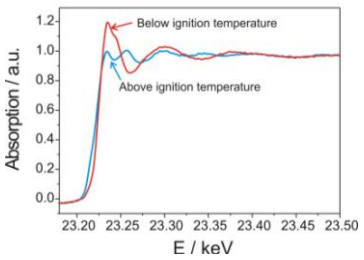


Grunwaldt, Hannemann, Schroer, Baiker, J. Phys. Chem. B 110, 8674 (2006).

X-ray absorption as function of X-ray energy

$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$





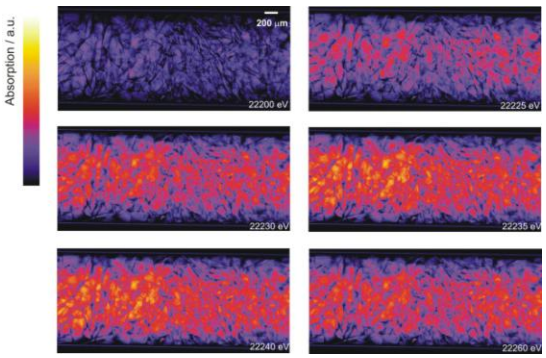
Sample:
2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He
ca. 400 °C

Grunwaldt, Hannemann, Schroer, Baiker, J. Phys. Chem. B 110, 8674 (2006).

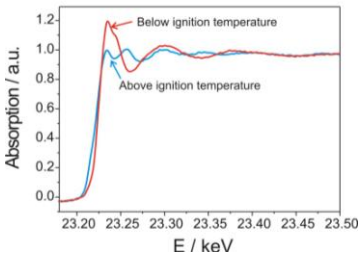
X-ray absorption as function of X-ray energy

$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$

Sample:
2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He



Absorption of X-rays behind capillary reactor at selected energies



Grunwaldt, Hannemann, Schroer, Baiker, J. Phys. Chem. B 110, 8674 (2006).

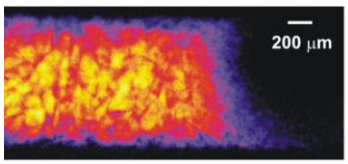
Result of full-field X-ray microscopy

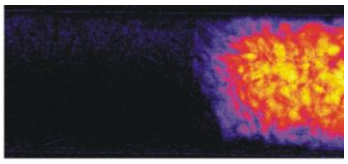
$CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$

Absorption by Rh^{3+}-component

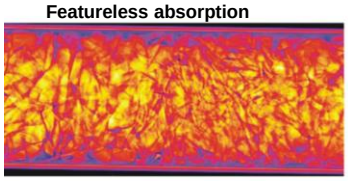
Absorption by Rh^0-component

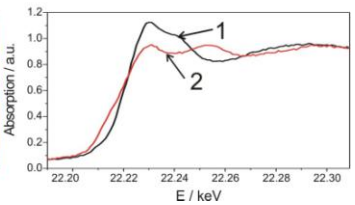
Inlet





Featureless absorption

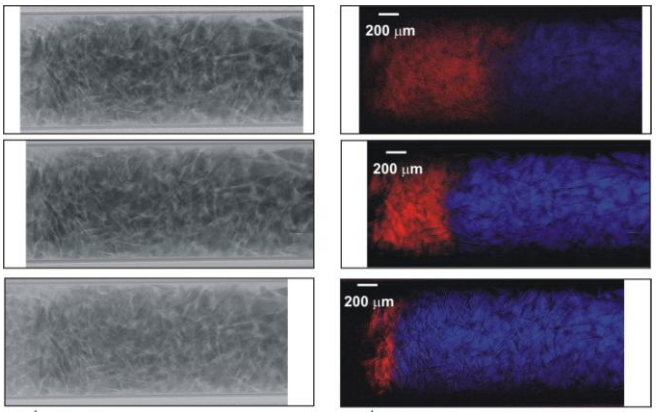




Gradient within 200 µm

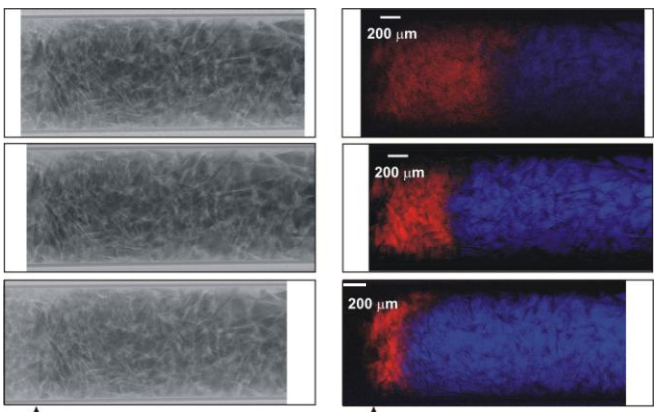
Grunwaldt, Hannemann, Schroer, Baiker, J. Phys. Chem. B 110, 8674 (2006).

Gradient as function of temperature (Rh K-edge)



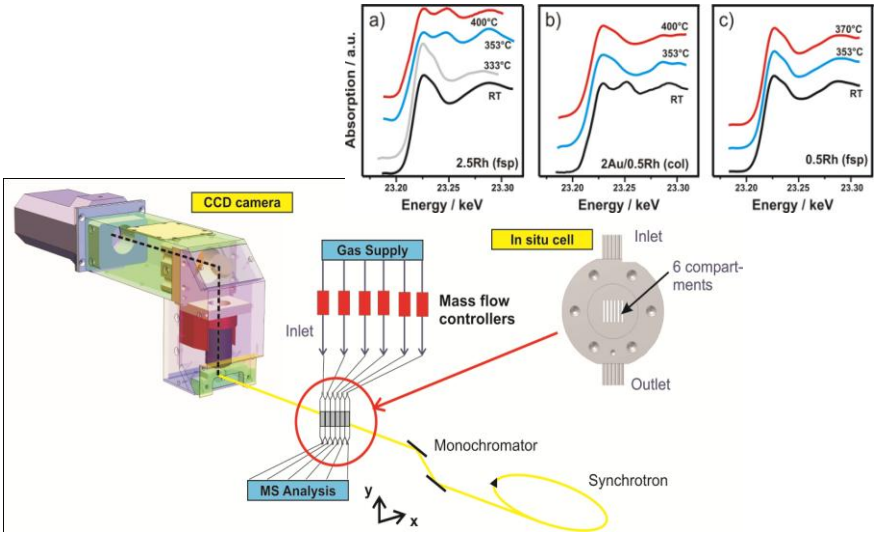
Sample:
2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He
14 mg, 12.5 ml/min

Gradient as function of space velocity (Rh K-edge)



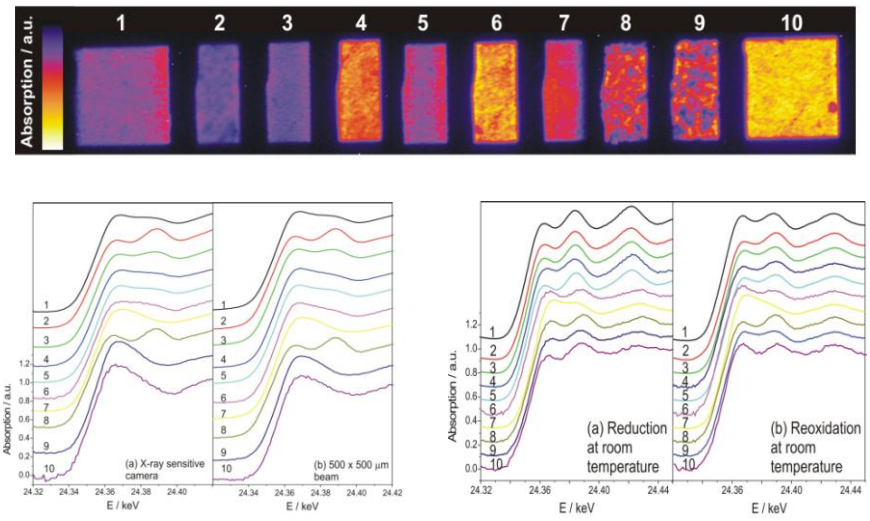
Sample:
2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He
14 mg, 12.5 ml/min

Catalysis and structure in parallel



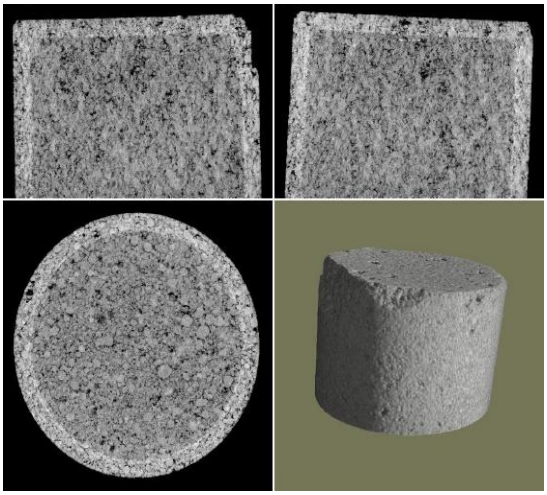
Kimmerle, Grunwaldt, et al., Appl. Catal. A 353, 36 (2010).

Perspectives: Parallel screening of Pd-based catalysts



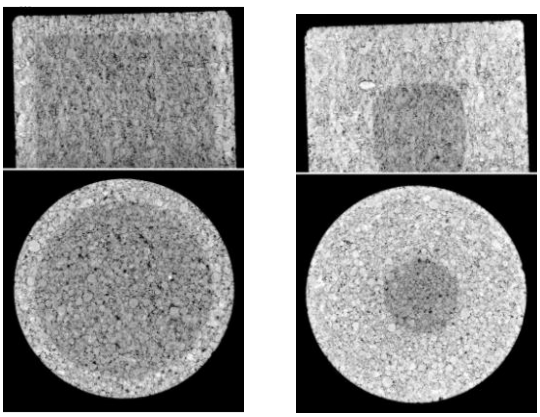
J.-D. Grunwaldt, B. Kimmerle, et al., J. Mater. Chem. 17, 2603-2606 (2007).

Going to the third dimension: X-ray tomography on shaped catalysts



3D-reconstruction of 0.5%Pd/Al_2O_3, shell-impregnated catalyst pellet of cylindrical shape; sample was stuck from one side on the sample holder, field of view: 3.54 mm x 2.36 mm; total reconstructed volume of 3.54 x 3.54 x 2.36 mm^3.

Going to the third dimension: X-ray tomography on shaped catalysts

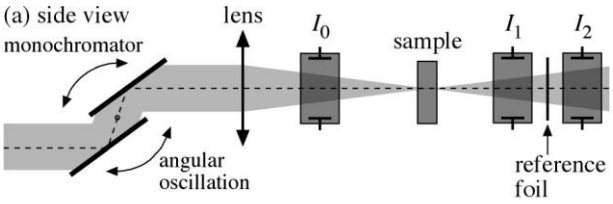


3D-reconstruction of Cu/Al_2O_3, (a) 1 min and (b) 10 min with $CuCl_2$-solution impregnated catalyst pellet; field of view: 3.54 mm x 2.36 mm.

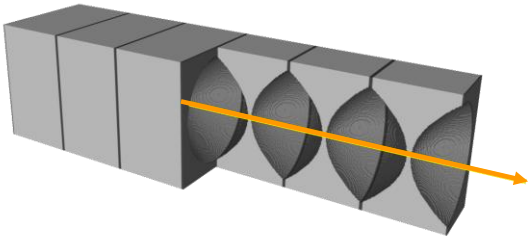
J.-D. Grunwaldt, et al., Catal. Today 145, 267 (2009).

Scanning X-ray absorption tomography

Experimental Setup



Stack of Be-lenses



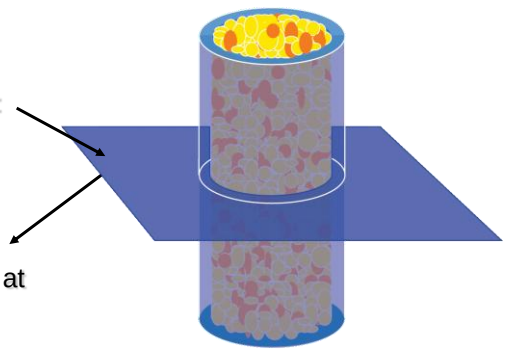
C. Schroer, B. Lengler, et al., Appl. Phys. Lett. 82, 1485 (2003).

Scanning X-ray absorption tomography

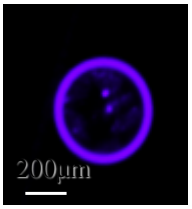
Sample:
CuO/ZnO catalyst + BN powder in glass capillary

virtual slice through sample:

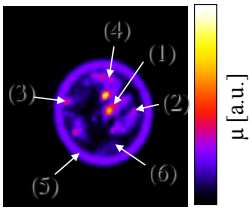
record absorption spectrum at each point

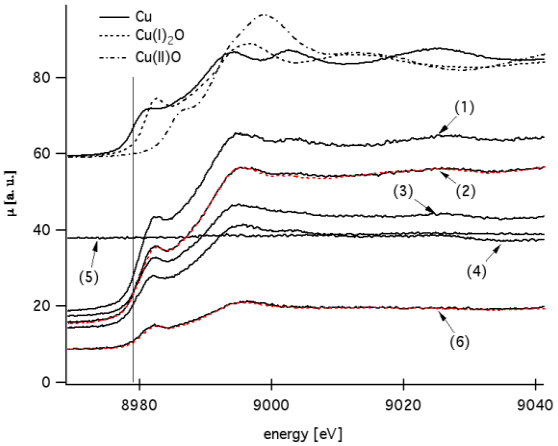


Scanning X-ray absorption tomography



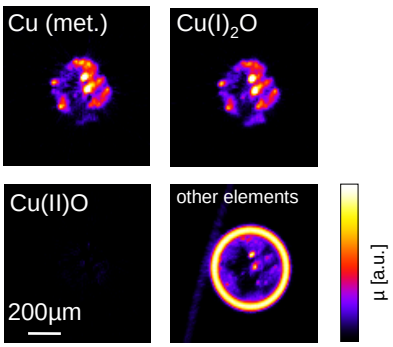
Above Cu K-edge

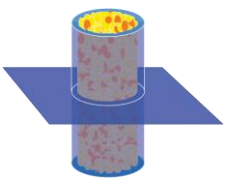




Scanning X-ray absorption tomography

XANES tomography:
Distribution of Chemical State

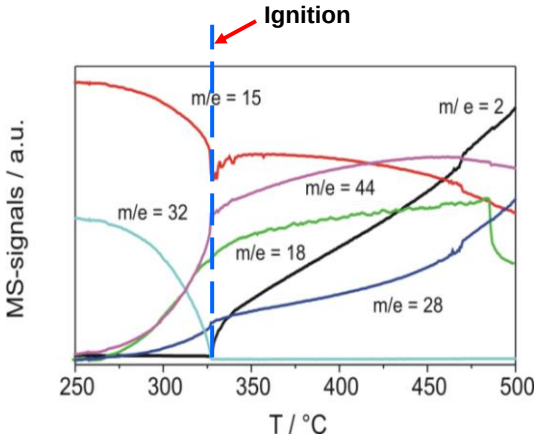




catalyst in capillary

Catalytic partial oxidation of methane: Ignition of the reaction

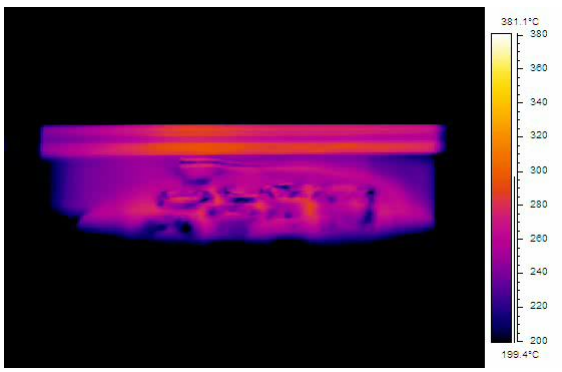
$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$



2.5%Rh-2.5%Pt/Al_2O_3, prepared by flame synthesis
6% CH_4, 3% O_2 in He, ramp rate: 5 K/min

Grunwaldt and Baiker, Catal. Lett. 99, 5 (2005).

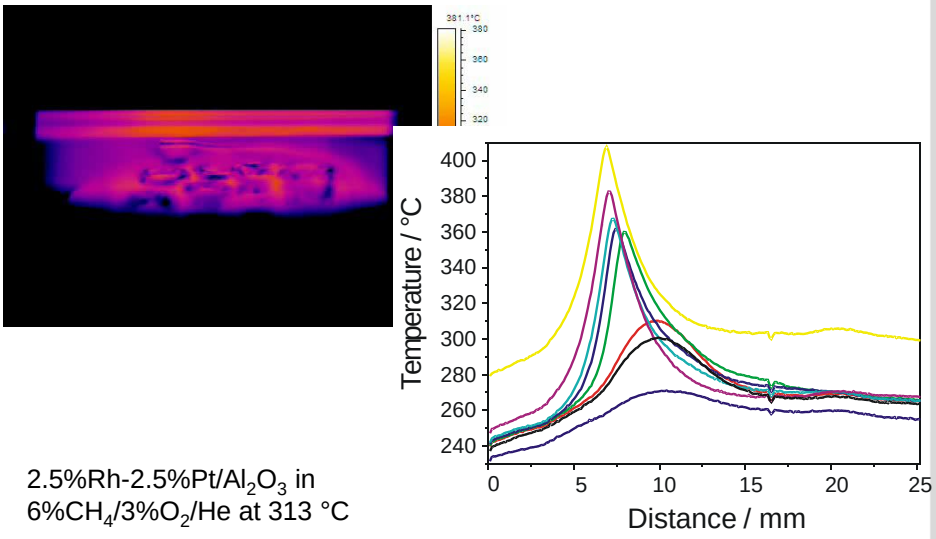
Temperature profile



2.5%Rh-2.5%Pt/Al_2O_3 in 6%CH_4/3%O_2/He at 313 °C

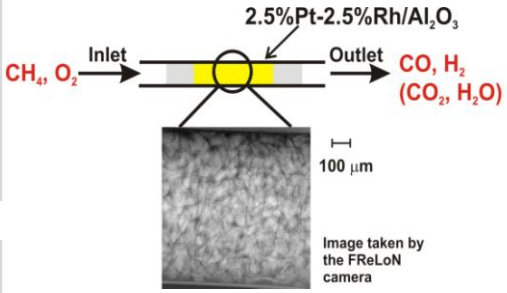
J.-D. Grunwaldt, et al., Catal. Today 145, 267 (2009).

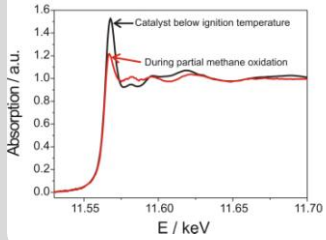
Temperature profile



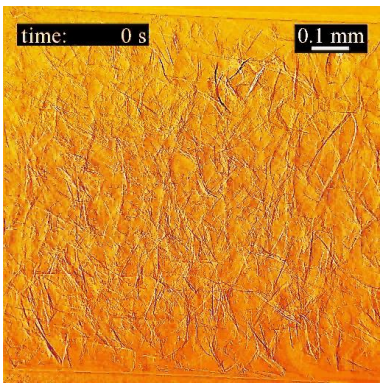
2.5%Rh-2.5%Pt/Al_2O_3 in
6%CH_4/3%O_2/He at 313 °C

Change of structure in a spatiotemporal manner



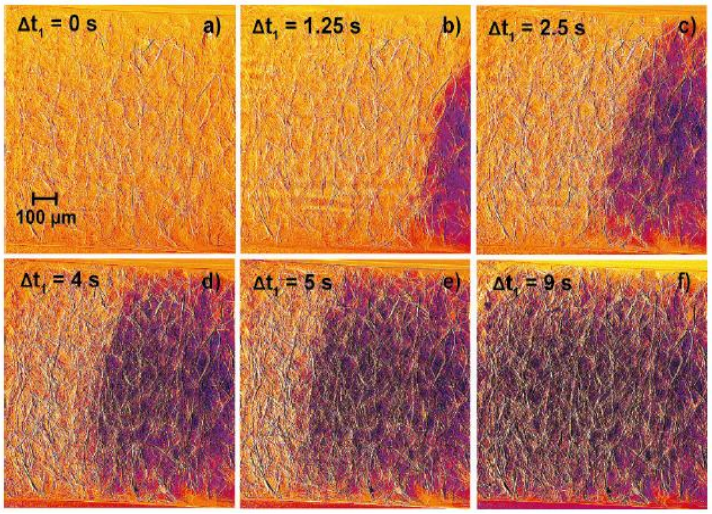


Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in
6%CH_4/3%O_2/He

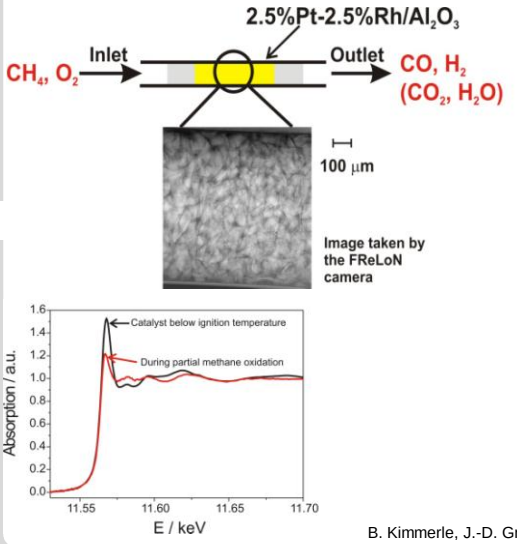


B. Kimmerle, J.-D. Grunwaldt, J. Phys. Chem. C (2009) Highlight at ESRF, 2009.

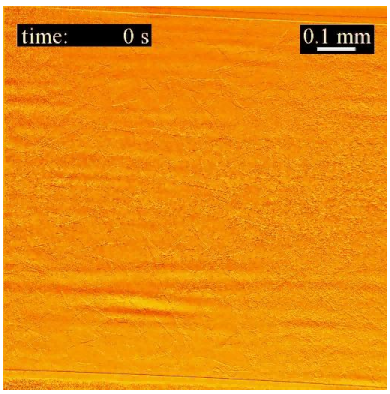
Change in structure during ignition



Change of structure in a spatiotemporal manner

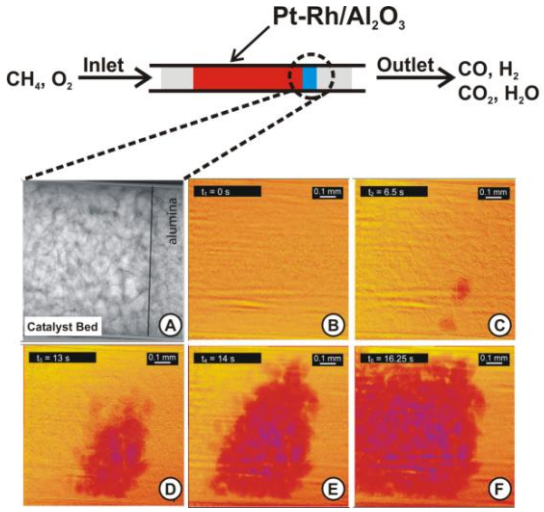


Sample:
2.5%Pt-2.5%Rh/Al_2O_3 in 6%CH_4/3%O_2/He

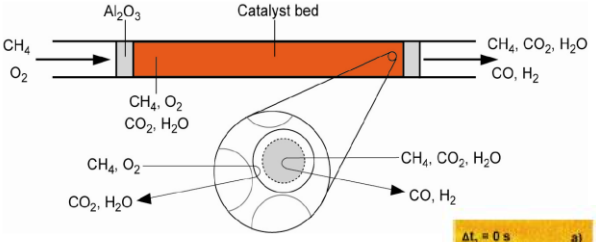


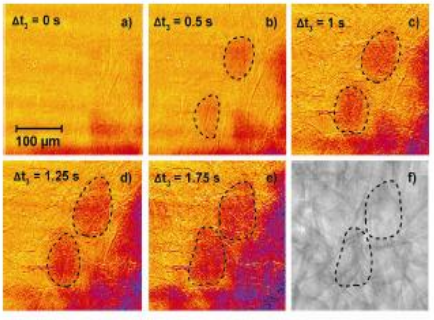
B. Kimmerle, J.-D. Grunwaldt, J. Phys. Chem. C (2009), Highlight at ESRF, 2009.

Processes occurring during the ignition



Processes occurring during the ignition of CPO





Summary and conclusions

- Dynamic & in situ studies are important for structural studies both on a micro- and nanoscale
- Hard X-ray based techniques advantageous for gas phase, high temperature, liquid phase and elevated pressure

- We need in future
  - Full EXAFS spectra
  - X-ray absorption tomography under in situ conditions
  - Better spatial resolution
  - Combination of full-field and scanning X-ray microscopy
  - Combination of electron and X-ray microscopy
  - Time-resolution with spatial resolution

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HASYLAB (Hamburg)

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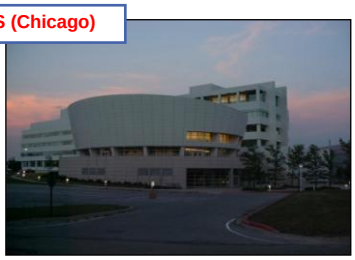

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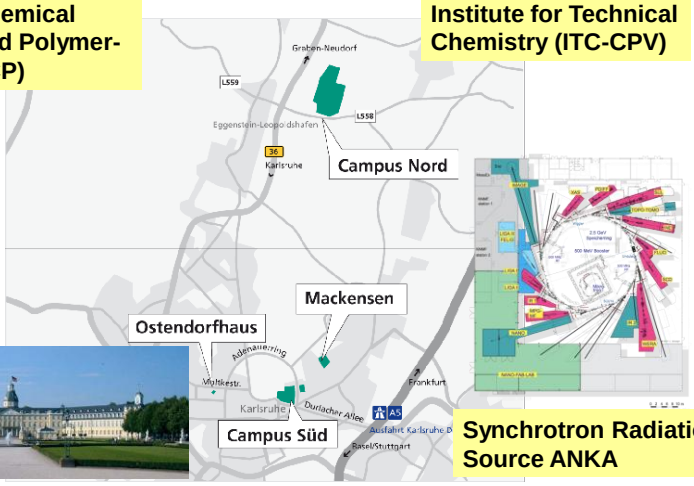
View on KIT

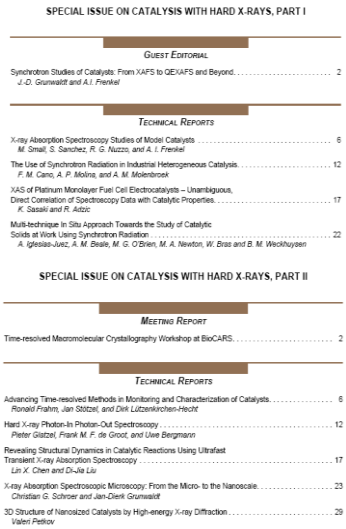
Institute for Chemical Technology and Polymer-Chemistry (ITCP)

Institute for Technical Chemistry (ITC-CPV)



Synchrotron Radiation Source ANKA

Final Remarks



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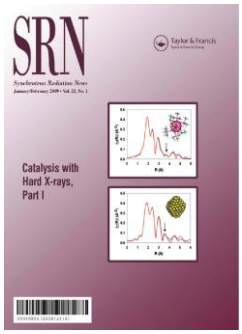

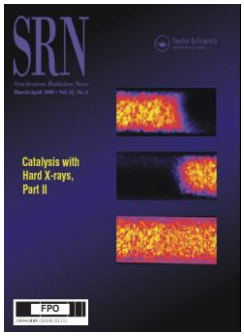

Two special issues edited by J.-D. Grunwaldt (DTU) and A.I. Frenkel (Catalysis Consortium, USA)

And: we are looking for **PhD and postdocs** at the interface of catalysis and in situ EXAFS and related synchrotron techniques!

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